



# Standard Test Method for Total Molybdenum in Fresh Alumina-Base Catalysts<sup>1</sup>

This standard is issued under the fixed designation D 3943; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of molybdenum in alumina-base catalysts and has been cooperatively tested at molybdenum concentrations from 8 to 18 weight %, expressed as  $\text{MoO}_3$ . Any component of the catalyst other than molybdenum such as iron, tungsten, etc., which is capable of being oxidized by either ferric or ceric ions after being passed through a zinc-amalgam reductor column (Jones reductor) will interfere.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

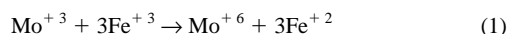
D 1193 Specification for Reagent Water<sup>2</sup>

E 173 Practice for Conducting Interlaboratory Studies of Methods for Chemical Analysis of Metals<sup>3</sup>

E 507 Test Method for Aluminum in Iron Ores by Atomic Absorption Spectroscopy<sup>3</sup>

## 3. Summary of Test Method

3.1 The catalyst is digested in hot sulfuric acid to dissolve molybdenum, destroy organic matter, and to expel nitrates if present. The acid solution is diluted and passed through an amalgamated zinc column (Jones reductor) into a receiving flask containing an excess of ferric ammonium sulfate. The column quantitatively reduces the molybdenum ( $\text{Mo}^{+6}$  to  $\text{Mo}^{+3}$ ) which in turn is reoxidized in the receiving flask according to the reaction:



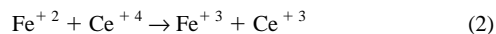
3.2 The ferrous ion produced (three per  $\text{Mo}^{+3}$  oxidized) is titrated with standard ceric sulfate solution in the presence of ferroin indicator. The indicator undergoes a color change (pink to colorless or very faint blue-green) in the presence of excess ceric ion. The amount of  $\text{Fe}^{+2}$  titrated in the reaction

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D 32.03 on Chemical Composition.

Current edition approved April 10, 2000. Published May 2000. Originally published as D 3943 – 80. Last previous edition D 3943 – 86 (1994)<sup>1</sup>.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 03.05.



is a direct measure of  $\text{Mo}^{+6}$  concentration.

## 4. Significance and Use

4.1 This test method sets forth a procedure by which catalyst samples can be compared either on an interlaboratory or intralaboratory basis. It is anticipated that catalyst producers and users will find this method of value.

## 5. Interferences

5.1 Elements such as As, Sb, Cr, Fe, Ti, V, U, or W can interfere in this analysis. If serious interference occurs, it will be necessary to isolate the molybdenum from the interfering species prior to measurement.

5.2 Organics and nitrates can interfere or react with the zinc-amalgam if the sulfuric acid treatment is not properly carried out as described in 9.1.

## 6. Apparatus

6.1 *Beakers*, 250-mL.

6.2 *Jones Reductor Column*, 30-cm long by 2 cm in outer diameter, with a 100-mL reservoir.<sup>4</sup> Attach a piece of vinyl tubing to the end of the delivery tube long enough to extend to the bottom of the filtering flask (see Test Method E 507).

6.3 *Vacuum Filtering Flask*, heavy-walled, 1000-mL.

6.4 *Buret*, 50-mL, Class A (0.1-mL divisions).

6.5 *Stirring Motor*, magnetic, and TFE-fluorocarbon-covered stirring bars, 7.9 by 14.2 mm ( $\frac{5}{16}$  by  $\frac{1}{16}$  in.).

## 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>5</sup> Other grades may be

<sup>4</sup> Part No. 8035-J10. The sole source of supply of this apparatus known to the committee at this time is Arthur H. Thomas Co. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup> which you may attend.

<sup>5</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

used provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

**7.2 Purity of Water**—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193.

**7.3 Ceric Sulfate**,<sup>6</sup> 0.10 *N* standardized using sodiummolybdate following the procedure given in Annex A1.

**7.4 Ferric Ammonium Sulfate Solution** —  $[\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}]$ —Dissolve 200 g of  $[\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}]$  in 1000 mL of water containing 20 mL of concentrated sulfuric acid. Add potassium permanganate solution dropwise until a pink color persists for 1 min.

**7.5 Ferroin Indicator**, 0.025 *M* solution of 1, 10-phenanthroline ferrous sulfate complex.<sup>7</sup>

**7.6 Jones Reductor Amalgam**.<sup>8</sup>

**7.7 Molybdenum Standard Solution**—Dissolve 1.0 g, weighed to the nearest 0.1 mg, of sodium molybdate dihydrate<sup>9</sup> ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) in water containing 10 mL of  $\text{H}_2\text{SO}_4$ , transfer to a 1-L volumetric flask, dilute to volume, and mix (1 mL = 0.5948 mg  $\text{MoO}_3$ ).

**7.8 Phosphoric Acid ( $\text{H}_3\text{PO}_4$ ), concentrated**—Mix 130 mL of concentrated  $\text{H}_2\text{SO}_4$  with 250 mL of water. Add the acid slowly with constant stirring. Add 140 mL of concentrated  $\text{H}_3\text{PO}_4$  and 15 mL of a saturated solution of  $\text{MnSO}_4$  (approximately 60 g/100 mL). Dilute to 1000 mL with water.

**7.9 Potassium Permanganate ( $\text{KMnO}_4$ )**, approximately 0.1 *M* solution.

**7.10 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ )**, concentrated, 1 + 1 and 1 + 19, dilutions with water, corresponding to 18 and 1.8 *N* solutions, respectively.

## 8. Sampling

**8.1** The selection of a representative analytical sample from the bulk material is outside the scope of the present method. It is presumed that parties using this test method for comparison purposes will have agreed on the selection of an analytical sample which is appropriate to their needs.

**8.2** Pulverize the analytical sample to pass a 150- $\mu\text{m}$  (No. 100) sieve. Ignite the pulverized sample for 30 min at 550°C in a muffle furnace. Allow to cool in a desiccator.

<sup>6</sup> Item No.  $\Delta$  SO-C-66. The sole source of supply of this reagent known to the committee at this time is Fisher Scientific Co. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup> which you may attend.

<sup>7</sup> Item No. P-69. The sole source of supply of this reagent known to the committee at this time is Fisher Scientific Co. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup> which you may attend.

<sup>8</sup> Item No. Z-18. The sole source of supply of this reagent known to the committee at this time is Fisher Scientific Co. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup> which you may attend.

<sup>9</sup> Item No. S-336. The sole source of supply of this reagent known to the committee at this time is Fisher Scientific Co. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup> which you may attend.

## 9. Procedure

**9.1** Transfer a 0.75-g specimen, weighed to the nearest 1 mg, into a 250-mL beaker. Add 20 mL of 1 + 1  $\text{H}_2\text{SO}_4$  solution and heat to fumes on a hot plate. Cool, rinse down with 10 mL of water and take to fumes again. Cool, add 100 mL of water and heat to dissolve. Cool to room temperature.

**9.2** Activate the Jones reductor by passive five 25-mL portions (1 min/25 mL of solution passed) of the 1 + 19  $\text{H}_2\text{SO}_4$  through the column, using slight vacuum. Do not allow the amalgam to become exposed to air. Test the column by passing a blank of 25 mL of 1 + 19  $\text{H}_2\text{SO}_4$  through the reductor into a receiver containing 15 mL of ferric ammonium sulfate solution. Add 2 to 3 drops of ferroin indicator and 10 mL of concentrated  $\text{H}_3\text{PO}_4$  and titrate with 0.1 *N* ceric sulfate solution until the pink indicator color completely disappears and is replaced by a colorless to faint blue green color which persists for at least 15 s. If more than 1 or 2 drops of ceric sulfate solution are required, repeat the washing and testing until a suitable blank is obtained.

**9.3** Pass the sample through the reductor into a receiver containing 25 mL of ferric ammonium sulfate solution and 10 mL of the concentrated  $\text{H}_3\text{PO}_4$ , using slight vacuum. Keep the tip of the reductor (extended by a piece of vinyl tubing) below the surface of the solution in the receiver.

**9.4** Rinse the reductor with five 25-mL portions of 1 + 19  $\text{H}_2\text{SO}_4$ , adding the washings to the receiver. Titrate the reduced iron solution in the receiver immediately with 0.1 *N* ceric sulfate solution using 2 to 3 drops of ferroin indicator. The faint blue-green color developed at the end point should persist for 15 s.

## 10. Calculation

**10.1** Calculate the percentage molybdenum as follows:

$$\text{MoO}_3 \% = (D - E)A/10w \quad (3)$$

where:

*D* = ceric sulfate solution required to titrate sample, mL,

*E* = ceric sulfate solution required to titrate blank, mL,

*A* = mg  $\text{MoO}_3$ /mL of ceric sulfate solution, and

*w* = dried weight of specimen, g.

**10.2** Calculate the arithmetic mean of each set of observations and report these values to two decimal places.

## 11. Precision and Bias<sup>10</sup>

**11.1** Eight laboratories participated in supplying data under the conditions outlined in Practice E 173. Statistical data calculated in accordance with this practice are recorded in Research Report D32-1020, along with standard deviations calculated by an alternative procedure.

**11.2** No reference standards were available to determine the bias of the test method.

## 12. Keywords

12.1 alumina-base catalysts (fresh); Jones Reduction; molybdenum

<sup>10</sup> Supporting data are available from ASTM Headquarters. Request RR:D32-1020.

**ANNEX**
**(Mandatory Information)**
**A1. STANDARDIZATION OF CERIC SULFATE SOLUTION USING SODIUM MOLYBDATE**
**A1.1 Standardization**

A1.1.1 Clean the Jones reductor thoroughly by passing repeatedly through it dilute sulfuric acid (1 + 19) and water until a satisfactory blank is established.

A1.1.2 Prepare a ferric ammonium sulfate solution, as described in 7.3 and transfer 25 mL of this solution to the receiving flask of the Jones reductor. Add 10 mL of concentrated phosphoric acid to the receiving flask. Prepare the phosphoric acid-manganous sulfate-sulfuric acid solution as described in 7.4 and transfer 10 mL to the same receiving flask of the Jones reductor.

A1.1.3 Be sure that the tip of the reductor dips well beneath the surface of the solution. Transfer 100 mL of the molybdenum standard solution (1 mL = 0.5948 mg MoO<sub>3</sub>) to a 250-mL beaker and add 20 mL of (1 + 1)H<sub>2</sub>SO<sub>4</sub>.

A1.1.4 With gentle suction, draw the molybdenum solution through the reductor, while gently swirling the solution in the receiving suction flask. Just before the surface of the liquid reaches the zinc, add 50 mL of cold H<sub>2</sub>SO<sub>4</sub>(1 + 19). Rinse the column twice more by adding 50 mL of water each time. Add

the water just before the surface of the solution reaches the zinc. Close the stopcock while a portion of the last rinsing remains in the reductor funnel. Disconnect and rinse the reductor as a little water is allowed to run through the stem, and rinse the outside of the stem. Titrate the collected solution with the ceric sulfate solution as described in 9.4. Correct for a reagent blank that has been carried through the entire procedure using the same amount of reagents.

**A1.2 Calculations**

A1.2.1 Calculate the molybdenum oxide equivalent of the ceric sulfate solution as follows:

$$A = B/(C - F) \quad (\text{A1.1})$$

where:

*A* = MoO<sub>3</sub>/mL of ceric sulfate solution,

*B* = molybdenum used expressed as mg MoO<sub>3</sub>,

*C* = ceric sulfate solution used in titration of the molybdenum, mL, and

*F* = ceric sulfate solution needed to titrate the blank, mL.

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